



Study of Electret State in Epoxyamine Polymers by Dielectric Spectroscopy

MANSUR GALIKHANOV,^{1,3} EKATERINA MOCHALOVA,¹
ILDAR GABDRAKHMANOV,¹ EDUARD GALIKHANOV,² IVAN LOUNEV,²
and YURII GUSEV²

1.—Kazan National Research Technological University, K. Marx, 68, Kazan, Russia 420015.

2.—Kazan (Volga region) Federal University, Kremlevskaya, 18, Kazan, Russia 420008.

3.—e-mail: mgalikhanov@yandex.ru

Electret and dielectric properties of polymer materials based on epoxy oligomer and polyamine amide were studied by dielectric spectroscopy. The orientation of the macromolecules polar groups in the electret state was shown to be fixed by a three-dimensional network, these groups acting as the charge. The electret state of the polymer matrix is a free state of epoxyamine macromolecules. Increased values of the thermoelectret hardness and tensile strength in comparison with those of non-polarized materials of the same composition proved the orientation of epoxy polymer segments.

Key words: Epoxy resins, electret, dielectric spectroscopy, relaxation processes, polarization

INTRODUCTION

Electrets are able to create a constant electric field without additional energy sources or high-voltage convertors, which is why they are used in modern high-tech devices. Polymers are widely used materials for electret production; therefore, their electret effect is well-studied.^{1,2} The most interesting polymer electret materials are those with three-dimensional network, which is because their structural features can have quite high and stable values of the electret characteristics. Application of the epoxy polymers for this purpose is known to be promising, and the number of papers concerning the study of electret effect in epoxide systems growing constantly.^{3–6} Their advantage is the possibility of comparatively easy change (enhance) of physical and mechanical properties of epoxy polymer materials via structural changes in an epoxy polymer three-dimensional matrix.⁷

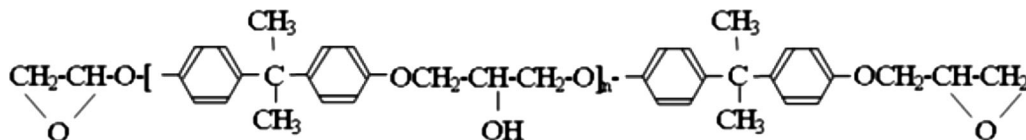
It was shown⁶ that combination of epoxy polymer synthesis and polarization processes allows obtaining thermoelectrets with controllable structure and properties. In particular, in the present work, the application of the electric field results in the orientation of oligomer molecular dipoles (polar groups, segments of oligomer chains). These dipoles are fixed by forming three-dimensional network inside the polymer. However, arguments are needed to prove this statement.

To study structure and properties of the different materials, including polymers, dielectric spectroscopy (DS) is widely used. Modern dielectric spectroscopy analyses the behavior of complex dielectric permittivity of studied materials in wide frequency and temperature ranges. It allows obtaining unique information about relaxation dynamics of a sample and to observe movements of separate molecules, molecular clusters and associates. Measurement of frequency and temperature dependence of dielectric properties is used for analyzing electret parameters of polymer materials.^{3,8–14} It makes sense since dielectric permittivity of a polymer depends on dipole and resonance polarizations while dielectric loss is defined by dipole-relaxation polarization.

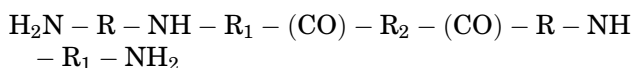
The purpose of the present paper is to study dielectric properties of epoxy polymers in order to describe their electret state.

MATERIALS AND METHODS

Epoxy oligomer DER-331 (Dow Chemical Company) with general chemical formula



and polyamine amide L-20 (60 mass parts to 100 parts of the resin) with formula



were chosen to be objects of the study.

Polarized samples (thermoelectrets) were obtained as follows. Epoxy polymer was cured in a special cell (Fig. 1) simultaneously with polarization in a constant electrical field caused by 5 kV voltage between electrodes, placed at a distance 1 mm from each other, for 2 h at a temperature of 110°C followed by cooling for 30 min with the field still on. Nonpolarized samples were obtained under the same conditions except the field application.

Electret parameters (surface potential, V_s , effective surface charge density, σ_{ef} , and electret field strength, E) were determined by periodic shielding of receiving electrode using a IPEP-1 field meter, measuring error not exceeding 3%.

Dielectric measurements were performed within the frequency range from 1 Hz to 1 MHz via dielectric spectrometer Novocontrol BDS Concept-80 with automatic temperature control using cryosystem QUATRO of $\pm 0.5^\circ\text{C}$ accuracy. The measuring cell is a plane-parallel capacitor with

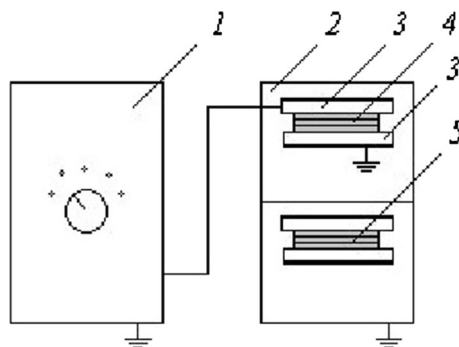


Fig. 1. Thermoelectret polarization unit: 1—high voltage generator, 2—furnace, 3—conductive plates, 4—polarized samples, 5—reference samples.

20 mm diameter gilded electrodes. Samples were 22 mm diameter, they were placed in the cell at room temperature. Measurements were performed in the temperature range of 260 K to 380 K with 5 K intervals. The dielectric permittivity measuring error is 3%. The principal scheme of dielectric measurements is shown on Fig. 2.

Dielectric experimental data handling was made using WinFit software. For numerical analysis of dielectric spectra Havriliak-Negami distribution function was used¹⁵:

$$\varepsilon^*(\omega) = \varepsilon_\infty \frac{\varepsilon_s - \varepsilon_\infty}{[1 + (i\omega\tau)^\alpha]^\beta}, \quad 0 < \alpha, \beta < 1,$$

where $\varepsilon^*(\omega)$ —complex dielectric permittivity; ε_s and ε_∞ —lower and upper frequency limits of dielectric permittivity, respectively; ω —angular frequency, Hz; τ —characteristic relaxation time, s; α and β —empirical exponents which describe symmetric and asymmetric expansion of the relaxation processes.

Phase transitions in the polymer were studied by differential scanning calorimetry (DSC) using Q-200TA calorimeter. The heating rate was 5 K/min.

Tensile strength σ_T of cured samples was measured by a tensile testing machine Inspekt mini TR-3 kN. Test bar cross section dimensions were 6×1 mm. Velocity of testing machine clamps movement was 50 mm/min. Shore D hardness HD was measured via durometer THS-200FJ.

RESULTS AND DISCUSSION

It is known that polymer electret surface potential, effective surface charge density and intensity of electrostatic field decrease rapidly during the first

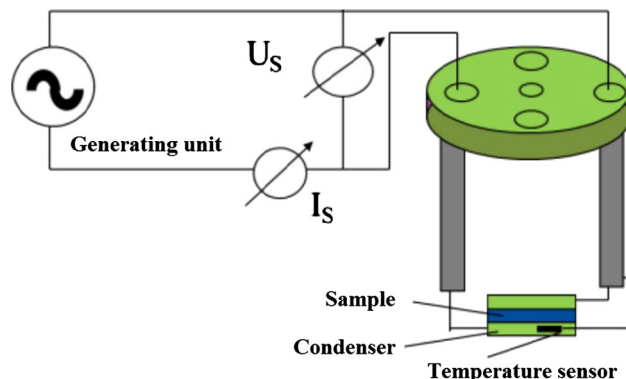


Fig. 2. Schematic diagram of dielectric permittivity measurement with Novocontrol BDS-80 spectrometer.

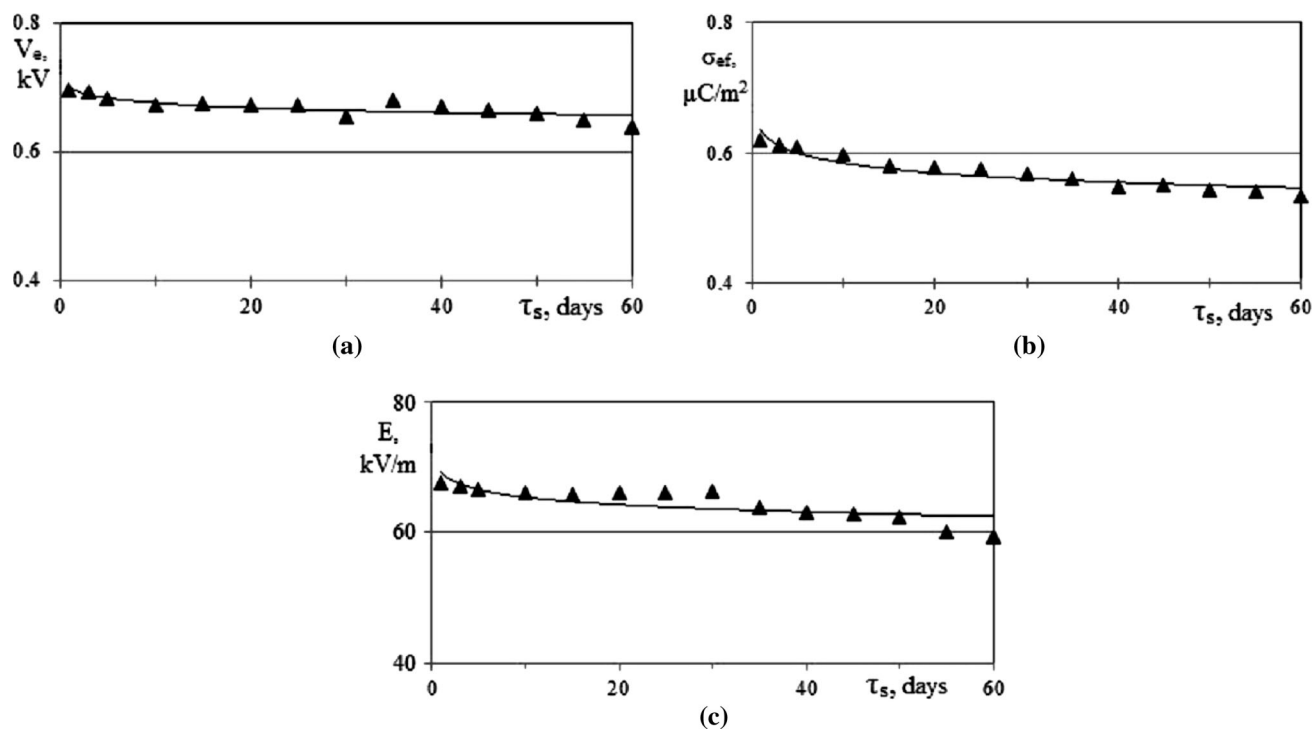


Fig. 3. Time dependence of surface potential (a), effective surface charge density (b) and electric field strength (c) of thermoelectret based on epoxy resin with curing agent.

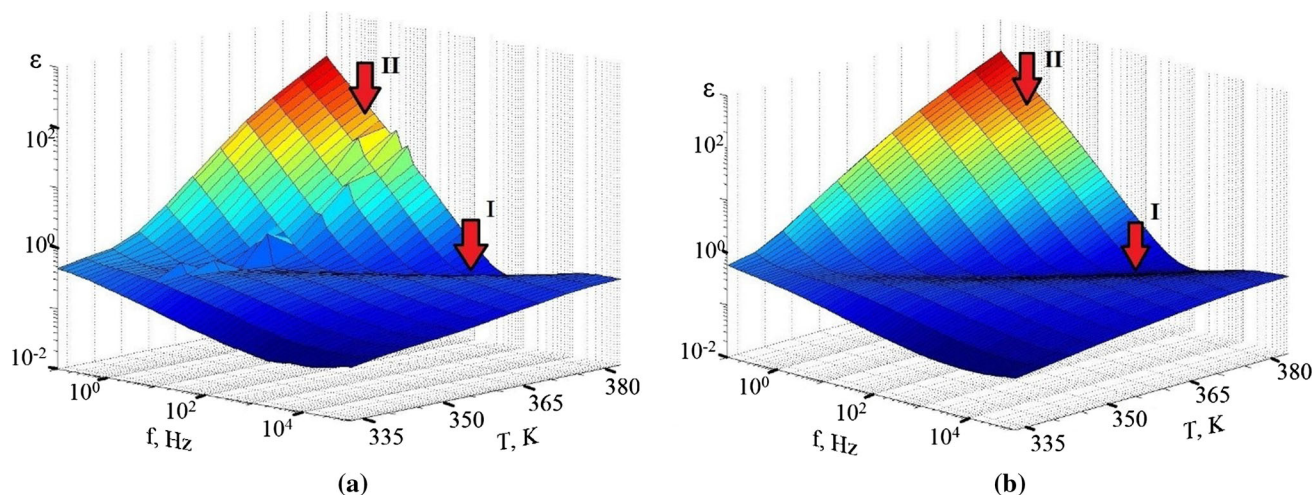


Fig. 4. Frequency and temperature dependence of dielectric losses for nonpolarized epoxy polymer (a) and thermoelectret on which it is based (b).

days after charging, then their values stabilize at a certain level. For thermoelectrets based on epoxy resin with curing agent, the following values of electret parameters were obtained: at the 60th day after charging $V_s = 0.64$ kV, $\sigma_{ef} = 0.35$ $\mu\text{C}/\text{m}^2$ and $E = 34.7$ kV/m (Fig. 3).

Study of epoxy polymers via DS technique (Fig. 4a) showed the presence of two relaxation processes. Experimental data handling by Havriliak–Negami method¹⁵ allowed estimation of relaxation energies of

these processes (Fig. 5). The first relaxation process with activation energy $E_{a1} = 243.2$ kJ/mole correlates with polymer transition from glassy to rubbery state. The second one with $E_{a2} = 170.4$ kJ/mole corresponds to post-cure reactions behavior, which accelerates with temperature.

To identify the processes occurring in the sample at the temperature increase, the polymer sample was studied via DSC (Fig. 6). An endothermic peak at the temperature range of 55–80°C and an

Table I. Hardness and breaking strength of non-polarized epoxy polymer (a) and thermoelectret on which it is based (b)

Characteristic	Non-polarized epoxy polymer	Thermoelectret based on epoxy polymer
H_D , c.u.	66.8	76.8
σ_T , MPa	33.9	41.8

The increase of tensile strength and hardness of the charged epoxy polymer may be explained by orientation of polar groups, which occurs under polarization of the samples. It results in the appearance of a more dense net of physical bonds and, consequently, in strength and hardness growth. Increase of strength properties of materials in electret state was observed before for both polymer and pulp-and-paper materials.^{2,6,18,19} Thus, increased values of strength and hardness of thermoelectrets in comparison with non-polarized materials of the same composition give indirect evidence of macromolecule segments orientation process which occurs during epoxy resin curing in electrical field.

CONCLUSION

Hence, polymer composites based on epoxy oligomer and polyaminoamide have high and stable electret properties. Herewith, dipole groups are “frozen” in cured net structure and mostly oriented in one direction. They are playing the role of the thermoelectret charge carriers. By using DS method we proved the orientation of dipole macromolecular groups of epoxy polymer material which is typical for polymer dielectrics with electret state. Calculation of dielectric relaxation process activation energy of the studied samples showed that electret state of the polymer matrix, formed during curing and fixed by chemical bonds of the three-dimensional network, is a free state of epoxyamine macromolecules. Increased values of thermoelectret hardness and strength in comparison with non-

polarized samples are also evidence of the orientation of epoxy polymer macromolecule segments.

CONFLICT OF INTEREST

We have no conflicts of interest to disclose.

REFERENCES

- G.M. Sessler, R. Gerhard-Multhaupt (eds.). *Electrets. 3rd edn. in two volumes* (Laplacian Press, Morgan Hill, California, USA, 1998/1999) 472/360 p.
- V.N. Kestelman, L.S. Pinchuk, and V.A. Goldade, *Electrets in Engineering: Fundamentals and Applications* (Boston: Kluwer Acad. Publ, 2000), p. 281.
- H. Smaoui, M. Arousc, H. Guermazi, S. Agnel, and A. Tourelled, *J. Alloys Compd.* 489, 429 (2010).
- V.N. Studentsov, E.A. Skudaeov, and R.V. Levin, *Int. Polym. Sci. Technol.* 41, 11 (2014).
- G.N. Nazmieva, T.A. Vakhonina, N.V. Ivanova, ASH Mukhtarov, N.N. Smirnov, A.V. Yakimansky, M. Yu, Balakina, and O.G. Sinyashin, *Eur. Polym. J.* 63, 207 (2015).
- E.N. Mochalova, N.A. Limarenko, M.F. Galikhanov, and R.Y. Deberdeev, *Polym. Sci. Ser. D* 9, 396 (2016).
- V.I. Irzhak and S.M. Mezhevikovskii, *Russ. Chem. Rev.* 78, 165 (2009).
- K. Mazur, *J. Phys. D Appl. Phys.* 30, 1383 (1997).
- M. Grimau, E. Laredo, A. Bello, and N. Suarez, *J. Polym. Sci.: Part B: Polym. Phys.* 35, 2483 (1997).
- P. Marin-Franch, D.L. Tunnicliffe, and D.K. Das-Gupta, *Mat. Res. Innovat.* 4, 334 (2001).
- M. Olszowy, *Condens. Matter Phys.* 6 2, 307 (2003).
- R.F. Suárez, A. Mellinger, M. Wegener, W. Wirges, R. Gerhard-Multhaupt, R. Singh, and I.E.E.E. Trans, *Dielectr. Electr. Insul.* 13, 1030 (2006).
- R.M. Neagu, E.R. Neagu, I.M. Kalogeras, and A. Vassilikou-Dova, *Mater. Res. Innovat.* 4, 115 (2001).
- C. Abdi, M.W. Khemici, and N. Douliche, in *Proceedings of 15th International Symposium on Electrets* (2014), pp. VIII.9.
- S. Havriliak and S. Negami, *J. Polym. Sci. Polym. Symp.* 14, 99 (1966).
- E. Galikhanov, I. Lounev, A. Guzhova, Yu Gusev, M. Galikhanov, and M. Vasilyeva, *AIP Conf. Proc.* 1722, 290002 (2016).
- A.A. Guzhova, I.V. Lounev, M.F. Galikhanov, YuA Gusev, M.A. Vasilyeva, and E.M. Galikhanov, *AIP Conf. Proc.* 1748, 020007 (2016).
- I.M. Vertyachikh, Y.I. Voronezhstsev, V.A. Goldade, and L.S. Pinchuk, *Plast. Massy* 3, 30 (1986).
- A.A. Perepelkina, M.F. Galikhanov, and L.R. Musina, *Surf. Eng. Appl. Electrochem.* 51, 138 (2015).

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.